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PAINT FAILURES ON RAN MINEHUNTER VESSELS: THE EFFECT OF SURFACE CONDITION ON ADHESION OF PAINTS TO IMMERSED GRP

L.V. WAKE AND R. CEKADA

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Paint Failures on RAN Minehunter Vessels: The Effect of Surface Condition on Adhesion of Paints to Immersed Glass Reinforced Polyesters

L.V. Wake and R. Cekada

MRL Technical Report MRL-TR-90-25

Abstract

The RAN Minehunter-Inshore vessels HMAS Rushcutter and HMAS Shoalwater have experienced paint blistering on immersed areas of the hulls of both ships. The hull surfaces are glass reinforced polyester (GRP) resin in a GRP-foam-GRP sandwich construction. Paint blistering has occurred from the inner hull surface in integral fuel and water tanks as well as from underwater areas on the outer hull surface. In view of the apparent degradation of the polyester in the tanks following coating failure, an investigation was carried out to determine the cause of the adhesion loss. Infrared examination of the failed areas showed the cause of paint detachment to be a poorly cured polyester layer under the paint. This layer softened on immersion in water or hydrocarbon fuel to the extent that it readily suffered mechanical damage. Fossible causes for the lack of cure of the surface polyester are discussed. Methods of treating the GRP to remove the uncrosslinked polyester layer were examined including sanding, sandblasting and chemical cleaning. Sandblasting was found to be the most effective surface treatment and significantly improved the adhesion of all paint coatings. Examination was also carried out to evaluate the effectiveness of alternative paint schemes including epoxy polyamide, epoxy polyamine (solventless), epoxy aminosilane, epoxy polyurethane and polyurethane formulations. The results showed that the polyurethane paints had excellent adhesion and were generally more tolerant of poor surface condition than solvent-borne epoxy pain's.

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Paint Failures on RAN Minehunter Vessels: The Effect of Surface Condition on Adhesion of Paints to Immersed Glass Reinforced Polyesters

1. Introduction

This report summarizes a series of investigations into the cause of paint blistering on the hulls of the two Minehunter-Inshore (MHI) vessels, HMAS Rushcutter and HMAS Shoalwater. Paint failures were first observed on the outer hull surface of MHI-01 (Rushcutter) in January 1987 at the time of its official launch. Blistering inside the hull was observed in the diesel tanks of MHI-02 (Shoalwater) in July 1987. Since that time, paint blistering has persisted in the tanks and to a lesser extent, on the underwater areas of both vessels. Inspection of the fuel and water tanks indicated that the paint had poor adhesion on all surfaces resulting in it detaching and bridging across the tank corners. The paint blisters were observed to be associated with mechanical disruption of a thin layer of polyester resin under the failed areas. The method of blister formation observed in this study is compared with reports of GRP failures elsewhere.

1.1 Summarized History of Paint Failures

The paint failures on the MHI vessels were initially addressed by Navy personnel at the shipyard and a short summary of their observations on the processes involved in the failures is as follows: "freshwater tanks, fore and aft trim tanks and PSU compartments were inspected on both vessels. Damage to all tanks below No. 2 tank was fairly typical, with the deterioration in the coating of the freshwater tank of HMAS Rushcutter at a more advanced state the coating in the freshwater tank of Rushcutter showed a marked loss of adhesion. The DO (diesel) tanks display a similar problem over 20% of their surface"....

"No failures have occurred in the topside paint systems despite quite heavy abuse during refit". "Extensive areas of the underwater system failed at the P/E (polyester/epoxy) interface. One patch of about 1 m² occurred under the slings of the HLV (heavy lift vehicle)". "The problems appear to be at the polyester/epoxy paint scheme interface. The paint schemes are epoxy based and generally employed following the application of a pretreatment primer (PTP)". "The MHCAT resin, which contains no wax additives in the isophthalic polyester resin is not fully cured for many days after gelation" and that "in many instances, when flakes of paint were peeled off, it came off at the interface and that the interface was still moist and tacky indicating incomplete cure at the polyester/epoxy (P/E) interface".

2. Blistering Mechanisms

2.1 Blister Formation in GRP Structures

The paint blistering described in this report differs in a number of aspects from osmotically driven "GRP blistering" (sometimes called "osmosis") frequently seen in immersed GRP laminates [1, 2]. The failures in the present study involve the loss of paint together with a thin film of polyester resin from the hull surfaces whereas the process of "osmosis" involves the formation of delaminations located between the gelcoat and the laminate and occasionally between the upper laminate layers. "Osmosis" is a widespread phenomenon and a considerable literature exists on its origins and causes [3-7]. No evidence of osmotic blistering was observed in this investigation.

The mechanism involved in "osmosis" is the result of water soluble components within the matrix driving the diffusion of water into the resin leading to blister formation. The paint failures, however, result from air inhibition of the polyester crosslinking reaction leading to a GRP surface with reduced crosslinks and greater permeability [8, 9]. Davis *et al* [10] have suggested that oxygen inhibition of polyester cure also causes excessive styrene evaporation from the surface and that this is aggravated by inhibitors or exceptional operating temperatures. A characteristic frequently reported with air-inhibited polyester resins is that they rapidly develop opacity in water [7].

2.2 Resistance to Blister Formation

Traditionally, polyester resins have been regarded as lacking chemical resistance because of the presence of the ester linkage. It has long been recognized [3, 11] that isophthalic resins provide superior blister resistance than orthophthalic resins and have formed the basis for the current British Plastics Federation (BPF) recommendations [12] on the use of these resins for boat hulls. In Australia the choice of isophthalic based resins for the Minehunter vessels stimulated their use in GRP hull construction in this country. The increased resistance of iso-based resins is a function of the reduced accessibility of the ester linkage to hydrolytic attack by water. Much success has been claimed [11] for these systems including

a matched approach using an iso-based gelcoat and an iso-based lay-up resin which has apparently produced blister free GRP boats for at least nine years. It is known that susceptibility of the ester linkage to hydrolysis is also reduced by increasing the size of the glycol unit [10], e.g. it is claimed [14] that the use of neopentyl glycol produces laminates with greater blister resistance because the two methyl groups provide steric protection of the ester linkage.

2.3 Use of Paint Coatings to Protect Immersed GRP Laminates

The dearth of publications on the protection of GRP and other plastics by the use of paint is surprising in view of the extensive literature on the painting of other substrates. Ghotra et al [15] have suggested that a barrier coating be used over the gelcoat in order to reduce the incidence of blistering. Evidence concerning the effectiveness of this procedure is inconclusive at present as a number of the coatings used for this purpose have themselves been observed to blister [7]. Marino et al [15] found that polyester paint coatings prevented blistering in gelcoated GRP although epoxy and polyurethane coatings blistered from the gelcoat. Epoxies, on the other hand, were found to be beneficial in preventing blister formation in the absence of a gelcoat. Relevant to this question was the observation by British dockyard workers [17] that the successful adhesion of epoxy paint to GRP was critically dependent on surface preparation.

3. MHI Hull Construction

3.1 Method and Materials of Hull Construction

The polyester material employed in construction of the MHI vessels was a chopped strand mat and woven roving glass reinforcement impregnated with isophthalic-based polyester resin (Cellobond A2785CV) [18]. Fourteen alternating layers (seven pairs) of chopped strand mat and woven roving were bonded and cured at 22 °C \pm 2 °C in a relative humidity of 65%. The resin was prepared and incorporated in an "un-waxed" condition. At the time of resin selection, it was claimed that cure of Cellobond AC2785CV would be inhibited but not stopped by air and that cure could be considered as optimum under the above conditions of temperature and humidity giving 99.0–99.5% cure for a correctly formulated resin after a period of 1 month [19].

The *in-situ* preparation of the GRP-foam-GRP sandwich for the hulls of the Minehunter vessels was carried out by applying the GRP to the outer surface of a 60 mm core of Divinycell H130 PVC foam which was held in place by wooden framework to the shape of the hull. On completion of the outer GRP layer, the frame was removed and the GRP bonded to the inner surface of the foam. In consequence, the two exposed GRP faces of the sandwich construction were air-contact cured. The outer air-contact cured hull surface faces the marine environment while sections of the inner hull surface are exposed to storage tank

solutions of fresh water, seawater and diesel oil.

The GRP panels used for this laboratory examination were prepared at Carrington Slipways by curing under the above conditions in metal trays which produced sheets with a woven textured air-cured upper surface and a flattened lower surface in contact with the tray. The panels were allowed to cure for several months before paint testing.

The concentrations of catalyst (methyl ethyl ketone peroxide) and promoter (cobalt octoate) for curing the polyester resin have been a matter of review throughout the MHI project. Initial recommendations [20] of 1–3% (vol/wt resin) of 0.6% cobalt octoate in styrene with 1.5–2.0% methyl ethyl ketone peroxide (MEKP) were altered because of short gel times which restricted laminating [20] during MHI construction. The level of catalyst chosen for laminating was 2% MEKP with a promoter level of 0.5% (vol/wt resin) of 1.25% cobalt octoate solution in styrene [13].

3.2 Painting of MHI Tanks

Painting of the MHI tanks has generally involved the application of a two-pack solvent based epoxy polyamine paint (International clear silicone epoxy paint 5224) over a GRP primer (sometimes referred to as a pretreatment primer or PTP). The GRP primer (International primer 78145) comprises an etching solution of methylene chloride containing an isocyanate which is said to react with the polyester hydroxyl groups in the GRP providing improved adhesion. One coat of the primer was applied followed by two thick coats (125 μm) of unpigmented epoxy polyamine. The formulations and procedures for application of this paint to the tanks were adapted from the method of painting the outer hull area of the MHI vessels (and of other GRP yachts). However, unlike the paints used externally on hulls, the paints used in the tanks were unpigmented so that failures in the underlying GRP/foam sandwich composite resulting from underwater explosions could be observed.

Following extensive blistering of the solvent based epoxy polyamine resin system in the tanks, a solventless epoxy polyamine paint (WEST System; Adhesive Technologies Pty Ltd) was employed on some tank surfaces without the pretreatment primer. In this scheme, the use of PTP was dispensed with by the RAN staff in view of the fact that "the bond strengths gained using PTP between the epoxy and polyester layers have been very poor" [13].

3.3 Painting of the MHI Outer Hull

The painting of the outer hull of the MHI vessels involved applying the pretreatment primer to the GRI and allowing it to cure for 24 hours. One coat of "Interfill" (International THB000/THA044), a low density epoxy filler, was applied over the GRP surface prior to painting with the "Hibuild". (The epoxy "Interfill" is solventless and provides a Larrier between the surface of the GRP and the solvents in the epoxy primer, believed by the dockyard staff to be the cause of softening in the polyester). This was followed by two coats of "Hibuild" (International) epoxy primer. An acrylic antifouling paint (International SPC) was then applied to the underwater areas to prevent marine fouling.

4. Experimental

4.1 Methods

The GRP panelling used for paint adhesion testing was analysed by Fourier Transform Infrared (FTIR) spectroscopy before and after surface treatments to remove undercured polyester material. Through-cure of the bulk polyester was analysed after sectioning of the panels.

Sections of the test panel $100 \text{ mm} \times 100 \text{ mm}$ were painted with a number of two-pack thermoset coatings to determine paint adhesion levels. One series of panels was examined for dry adhesion while others were immersed in water or diesel fuel and the adhesion measured following removal from the test solution. The paints were tinted with a clear red dye, "oil red O", added to a final mixed ratio of 140 mg/L.

All paints were spray applied except for the solventless epoxy system which was too viscous for spray application. This paint, which had a highly exothermic cure and set in less than 20 minutes, was brush applied. Following paint cure, the panels were immersed in either water or diesel fuel for a period of 20 days. At the end of the immersion period, the degree of discoloration (opaqueness) of the GRP under each paint was determined.

Adhesion testing on the panels which had been immersed was carried out by glueing dollies to the paints and measuring coating adhesion with an Epprecht "Twistometer" which determines the torque necessary to remove the dolly. Where cyanoacrylates glues were used for test, the adhesion level was determined 30 minutes after removal from the immersion tank, whereas two-part epoxy glues required dry curing for 3 days.

4.2 Paints

The paints examined in this report are shown in Table 1.

Each of the paints evaluated in the present trial is a readily available commercial material. Polyurethanes 1, 2 and 3 differed from each other as follows: polyurethane 1 is a flexible polyurethane, polyurethane 2 is a rigid highly crosslinked material and polyurethane 3 is a flexible polyurethane with filler.

5. Results

5.1 Degree of GRP Cure

The results of FTIR examination of the polyester before and after surface treatment are shown in Table 2. It is apparent that the air-contact cured GRP surface contains undercured polyester resin.

Table 1: Thermoset Paints Applied to GRP

No.	Paint	Manufacturer	Code
1.	Polyurethane 1	Paint Industries Pty Ltd	PU1
2.	Polyurethane 2	Paint Industries Pty Ltd	PU2
3.	Polyurethane 3	Paint Industries Pty Ltd	PU3
4.	Desmodur L/Desmophen 1100	Bayer Pty Ltd	DL
5.	Silicone epoxy 5224 curing agent 5224	International (Taubmans)	INT
6.	Solventless epoxy bisphenol F	Adhesive Technol (West Pty Ltd)	WEST
7.	Epoxy polyurethane	Paint Industries Pty Ltd	IFTC
8,	Epoxy aminosilane	Paint Industries Pty Ltd	EA
9.	Epoxy aminosilane/polyamide	Paint Industries Pty Ltd	EAP
10.	Epoxy polyamide	Paint Industries Pty Ltd	EP

Table 2: Results of FTIR Analysis of GRP

Pretreatment	Cure	Styrene Crosslinks
No Treatment		
Top Surface	Negligible	0%
Bulk	Present	100%
Back Surface	Present	100%
Methylene Chloride etch of top surface	Negligible	0%
Methylene Chloride etch + isocyanate pretreatment	Negligible	0%
Sanding (top)	Present	20%
Sandblasting (top)		
250 KPa	Present	30%
300 KPa	Present	50%
300 KPa (x 2)	Present	65%

The GRP surface layer softened after short term immersion in water or solvent. The surface layer also changed colour in water forming an opaque surface film which appeared slightly thicker (ca. $100\,\mu m$) than each of the paint coatings

covering it. The degree of discoloration (opaqueness) of this layer under each paint is shown in Table 3. On drying, the white opaque layer retained its colour but became powdery in texture.

Table 3: Opaqueness of GRP in Water

Paint	Opaqueness*
Uncoated	5
Epoxy Polyamide	4 +
Silicone Epoxy	3
Solventless Epoxy	1 +
Epoxy Aminosilane	5
Epoxy Aminosilane/polyamide	4 +
Polyurethane (1)	3 +
Polyurethane (2)	4
Polyurethane (3)	4
Epoxy Polyurethane	1 +

^{*} Opaqueness or water discoloration was measured as follows: 0 = unchanged; 5 = most opaque

Infrared examination of the polyester showed no increase in styrene crosslinks with solvent etch treatment. Mechanical treatments, such as sanding and sandblasting were found to be more effective for removing undercured polyester. However sanding was unable to remove the uncrosslinked material in depressions of the textured surface. Sandblasting of the GRP surface with increasing pressures progressively increased the level of styrene crosslinks across the textured surface. This technique was not restricted by surface profile.

5.2 Dry Adhesion Testing

The results of the dry adhesion testing are shown in Table 4. Note the higher adhesion strengths obtained for paint on the textured but uncrosslinked polyester surface (0% styrene crosslinks) than that on the smooth but crosslinked side (100% styrene crosslinks). The results show an increase in dry alhesion of paint to all panel surfaces following sandblasting.

Table 4: Adhesion Tests — Dry Panel Adhesion (KPa.cm²)

Paint	Front Panel	Front Sandblast	Back Panel	Back Sandblast
PU1	>250	>240	190 AF	275 (CF 50%)
	>230	>230	155 AF	190 (CF 50%)
	>230	>220	180 AF	,
PU2	190 AF	> 170	140 (CF 20%)	220 (CF 20%)
	170 AF	> 200	170 (CF 25%)	200 CF
	190 AF	> 190	170 (CF 25%)	220 CF
PU3	200 (CF 90%)	> 200	200 CF	220 CF
	240 (CF 70%)	> 170	190 CF	200 CF
	230 (CF 90%)	> 200		
EP	120 (CF 50%)	120 (CF 50%)	70 AF	215 CF
	100 (CF 80%)	105 (CF 50%)	110 AF	250 AF
	105 (CF 80%)	100 (CF 30%)	110 AF	265 CF
EAP	150 AF	> 225	170 AF	260 AF
	160 AF	> 255	260 AF	250 AF
	170 AF	> 230	190 AF	220 AF
IFTC	215 (CF 90%)	> 200	190 (CF 90%)	100 CF
	190 (CF 20%)	> 190	150 AF	100 CF
	180 (CF 20%)	> 190	100 AF	100 CF
INT	100 AF	230 (CF 25%)	160 AF	250 AF
	100 AF	230 (CF 25%)	170 AF	230 AF
	100 AF	220 (CF 50%)	150 AF	210 AF
WEST	265 (CF 50%)	> 265	275 AF	290 (CF 20%)
	260 (CF 50%)	> 250	205 AF	240 (CF 20%)
	270 (CF 50%)	> 270	280 AF	300 (CF 20%)

Code

CF indicates cohesive failure of the coating.

5.3 Immersion Testing

The results of paint adhesion testing on immersed GRP panels are shown in Tables 5 and 6. Extremely large decreases in adhesion are apparent when compared with the dry adhesion levels, reductions commonly being of the order of 60–80%.

Paint adhesion on immersed panels improved three to fourfold on sandblasted panels when compared with nonblasted panels and approached the adhesion levels achieved with dry panels. The colour change of the surface

> indicates glue failure between the test dolly and the paint.

AF indicates adhesive failure between the paint and substrate.

layer of unblasted panels on immersion was not observed when these were sandblasted. All paints gave satisfactory adhesion on the sandblasted panels although the adhesion of the epoxy polyamide coating was significantly lower than other paints. Repeated sandblasting showed no additional improvement in adhesion on immersed panels compared to panels which had been sandblasted once, in spite of the increased level of styrene cross-linking in the GRP substrate.

Table 5: Paint Adhesicn After Water Immersion

Paint	Front	Front Sandblast	Back	Back Immediate
PU1	50 (CF 50%)	> 250	70 AF	NT
	50 (CF 50%)	> 280	105 AF	
	60 AF	> 240	80 AF	
PU2	35 AF	> 295	230 AF	40 (CF 30%)
	50 AF	> 280	110 AF	20 (CF 50%)
	80 AF	> 310	170 AF	30 (CF 50%)
PU3	75 AF	> 305	185 AF	95 AF
	85 AF	> 340	145 AF	80 AF
	100 AF	> 320	120 AF	
EP	0 AF	> 130	80 AF	25 (CF 20%)
	0 AF	> 140	70 AF	50 AF
	0 AF	> 140	90 AF	15 (CF 40%)
EAP	45 AF	> 275	125 AF	110 AF
	40 AF	> 250	140 AF	150 AF
	30 AF	> 250	125 AF	100 AF
EA	10 AF	> 150	100 AF	50 (CF 80%)
	10 AF	> 170	65 AF	50 (CF 70%)
	10 AF		75 AF	
IFTC	100 AF	> 330	95 AF	15 (CF 40%)
	70 AF	> 340	90 AF	20 (CF 50%)
	70 AF	> 320	130 AF	30 AF
INT	0 AF	> 250	90 AF	80 AF
	0 AF	> 270	105 AF	60 AF
	0 AF	> 290	120 AF	40 AF
WEST	> 95	> 310	175 AF	90 AF
	100 AF	> 300	165 AF	110 AF
	100 AF	> 310	150 AF	70 (CF 50%)

The adhesive paint failures of nonblasted painted panels were observed to be associated with disruption of the opaque polyester layer under the paint. Examination of the paint coatings showed that they were clear, tough and resilient, but that the disrupted panelling (small pieces of which remained

adhering to the underside of the paint) was soft and gel-like. Infrared examination of the failed material showed it to be uncrosslinked polyester. The degree of colour change of the GRF under each paint corresponded roughly with the degree of adhesion loss, e.g. the smaller colour changes of the GRP under more highly crosslinked paints such as the solventless epoxy and the non-flexible polyurethane coatings approximately corresponded with improved adhesion.

Table 6: Paint Adhesion After Diesel Immersion

Paint	Front	Front Sandblast	Back	Back Immediate
PU1	> 120	> 235	100 AF	105 AF
		> 250	109 AF	110 AF
		> 250	120 AF	
PU2	70 (CF 50%)	> 240	190 AF	120 AF
	100 (CF 20%)	> 220	225 AF	> 120
		> 225	185 AF	
PU3	130 AF	> 220	115 AF	50 AF
	150 AF	> 2.50	115 AF	110 AF
		> 200	120 AF	
EP	100 AF	200 AF	40 AF	90 AF
	110 AF	170 AF	50 AF	60 AF
	110 AF	160 AF	50 AF	
EA	30 AF	> 180	145 AF	110 (CF 10%)
	65 AF	> 170	110 AF	110 (CF 10%)
			145 AF	
EAP	125 AF	> 275	115 AF	> 180
	130 AF	> 250	115 AF	
	35 AF	> 250	110 AF	
IFTC	70 AF	> 250	100 AF	100 AF
	70 AF	> 280	105 AF	120 AF
		> 265	115 AF	
INT	0 AF	> 220	110 AF	130 AF
•	0 AF	> 220		100 AF
	0 AF	> 220		90 AF
WEST	90 AF	> 225	120 AF	130 (CF 25%)
	105 AF	> 250	210 AF	100 (CF 25%)
		> 230	160 AF	,

6. Discussion

Paint adhesion to the GRP panel was found to be satisfactory providing that the scheme was maintained in a dry condition. Dry paint adhesion was lowest for the epoxy polyamide and International silicone epoxy paints while the polyurethanes and solventless epoxies were found to have excellent adhesion. For the polyurethanes, the isocyanate groups are known to be capable of reacting with hydroxyl groups in the polyester while the solventless epoxies presumably do not adversely affect the substrate by swelling to the same extent as with the solvent-borne paints.

However, large decreases in paint adhesion were obtained following immersion of the GRP panels. The inability to obtain a bond strength (zero readings) for the air-contact cured immersed surface, painted with International silicone epoxy in both water and diesel fuel corresponded to the in-Service performance of this paint in the MHI tanks, i.e. paint adhesion failure.

The first indication of the cause of this reduced adhesion strength was that the immersed panels formed a whitish opaque surface layer. This observation was similar to that described by Abeysinghe et al [7] on the effects of water on air inhibited polyesters. A lack of styrene crosslinks in the surface layer was confirmed by infrared examination which also showed that styrene levels increased with depth from the surface (Table 2). The undercure in the surface layer suggests that a phenomenon has occurred resulting from air inhibition and styrene loss. As the GRP laminate is relatively hard under dry conditions, it would appear that although crosslinking has been inhibited, some degree of chain extension has occurred.

The application of paints reduced, but did not prevent, the formation of opacity in the surface layer of polyester on immersion testing.

Abeysingle et al [7] reported that the opaque film appears as a foam-like layer under scanning electron microscopy. Rosen [21] attributed this opacity to microfracture, Barrer and Barrie [22] to microvoid formation while Pantony [23] believed that it was due to hydrolysis. Abeysinghe et al [7] reported that the opacity disappeared after short term immersion but is retained after longer immersion periods. In the present investigation, the opacity gradually appeared after an immersion period of 5 days in water. However, when the panel was acetone-wiped before water immersion, the opacity appeared within 2 hours. The acceleration in opacity formation is presumed to reflect the increased swelling of the polyester following solvent exposure.

The question of appropriate conditions and formulation requirements to ensure cure of the polyester resin used in the MHI hull has been a matter of concern throughout the planning and production phases of the project. The area of chief concern has been the choice of suitable levels of catalyst and promoter, sufficient to obtain cure without the production of too great an exotherm. Excessive heat production during cure is liable to cause brittleness and microcracking. It was decided [20] that an exotherm maximum of 25 °C over initial resin temperature not be exceeded.

The cause of surface undercure remains a matter of contention and a number of factors may be involved. Cellobond A2785CV is a high molecular weight polyester resin for which the local supplier [18] originally recommended that wax was not required for cure (Section 2.1). Following recognition of the lack of surface cure, the use of wax was recommended by the local supplier [24]

contrary to earlier advice. It was also suggested that the gel times (1.5–2.0 h) were too slow for cure of the surface layer of polyester as it would permit excessive styrene evaporation resulting in undercure. An enquiry at this time to the overseas manufacturer [25] nevertheless reaffirmed the use of the resin in an unwaxed condition as originally recommended. Tests on this resin material, however, showed that samples previously prepared without wax and held in the laboratory, all showed surface sensitivity to acetone.

The repair of undercured polyester surfaces to obtain adequate adhesion has been shown to require mechanical treatment in addition to solvent treatment [17]. Jackson [26] also observed that mechanical treatments gave improved adhesion and that of these, sandblasting provided the best results.

Two separate procedures were adopted for repair of the freshwater and diesel fuel tanks of the MHI vessels. The reason for the different approaches to repair of the tanks is that while the cured isophthalic GRP will be resistant to freshwater, the resin is known to be sensitive to the alkoxy ether fuel additives in the diesel fuel tanks. This sensitivity necessitates the use of a paint resistant to the fuel and its additives.

The repair scheme adopted for the MHI freshwater tanks incorporated a wax into the resin as follows:

MEKP	15 ml
cobalt octoate (0.6% wt/vo!)	25 ml
wax (5% wt/vol)	25 ml
Cellobond	1 kg

The repair procedure in the freshwater tanks involved sanding the GRP surfaces to remove undercured resin followed by a styrene wipe prior to laminating with surface tissue and the waxed polyester resin. The cure times with this resin system are less than the two hours schedule involved in the hull matrix but are necessary to overcome the reduced exotherm involved in curing the relatively thin layer of resin at the surface. Test panels of GRP prepared with the above formulation were not sensitive to acetone.

The repair scheme adopted for the diesel tanks involved surface sanding to remove undercured resin followed by patching damaged areas with a layer of chopped strand mat/woven rovings. Surface tissue/waxed resin was applied to the tank surface as above, degreased, post cured for two days and two coats of Anthozane (459-9006/455-9007) applied for surface protection.

At the present time, tank repairs using the above approach are reported to be performing satisfactorily.

7. Conclusions

(1) A thin layer of polyester at the GRP surface has been shown by FTIR examination to be undercured. This surface, which was cured by air contact, formed an opaque layer after immersion. Other investigations on GRP failures have reported similar findings. It is known that air inhibition of surface cure leads to reduced crosslinking and higher permeability to water because of inadequate crosslinking.

- (2) Paint adhesion failures on GRP panels immersed in water or diesel fuel were characterized by mechanical failure of the undercured polyester surface layer. Paint adhesion levels fell significantly following immersion. Polyurethanes were found to be more tolerant of poor surface condition than epoxy paints.
- (3) Sandblasting was found to be the most effective surface treatment for the removal of undercured polyester from the GRP panels. Paint adhesion on sandblasted panels was increased by 300–600% over unblasted panels on immersion testing.

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Glass reinforced plastic Adhesion Coatings
Cure Blister formation Paints

SUBJECT GROUPS

ABSTRACT

The RAN Minehunter-Inshore vessels HMAS Rushcutter and HMAS Shoalwater have experienced paint blistering on immersed areas of the hulls of both ships. The hull surfaces are glass reinforced polyester (GRP) resin in a GRP-foam-GRP sandwich construction. Paint blistering has occurred from the inner hull surface in integral fuel and water tanks as well as from underwater areas on the outer hull surface. In view of the apparent degradation of the polyester in the tanks following coating failure, an investigation was carried out to determine the cause of the adhesion loss. Infrared examination of the failed areas showed the cause of paint detachment to be a poorly cured polyester layer under the paint. This layer softened on immersion in water or hydrocarbon fuel to the extent that it readily suffered mechanical damage. Possible causes for the lack of cure of the surface polyester are discussed. Methods of treating the GRP to remove the uncrosslinked polyester layer were examined including sanding, sandblasting and chemical cleaning. Sandblasting was found to be the most effective surface treatment and significantly improved the adhesion of all paint coatings. Examination was also carried out to evaluate the effectiveness of alternative paint schemes including epoxy polyamide, epoxy polyamine (solventless), epoxy aminosilane, epoxy polyurethane and polyurethane formulations. The results showed that the polyurethane paints had excellent adhesion and were generally more tolerant of poor surface condition than solvent-borne epoxy paints.